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## Technology Development and Operation Experience for Anionite AV-17-8 with Improved Kinetic Properties

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### Abstract

Data are presented concerning the technology employed for anionite AV-17-8 industrial production as compared to the technology developed at the Kemerovo Azot JSC, as well as an experience is described concerning the operation of AV-17-8 anionite manufactured according to a novel technology, with improved kinetic properties at the stage of finishing water purification in a water treatment plant.

**Key words:** anionite AV-17-8, quality, application, production

### INTRODUCTION

Almost all thermal and nuclear power stations involve a closed steam power cycle in order to transform thermal energy into electric energy. The process of water purifying from impurities, as a rule, is performed with the application of ion-exchange resins, in particular, a classical anionite AV-17. At the same time, the necessity for optimizing the operation of a water treatment plant (improving the quality of produced water and steam, the condition of equipment, decreasing the consumption of reagents for regeneration, increasing the filtration cycle even to silicic acid breakthrough, diminishing the volume of washing water after regeneration) determines the urgency of studies concerning the development of more efficient anionite.

Within the framework of solving this problem we have proposed a technology for producing high-quality anionite AV-17-8 with improved kinetic and mechanical properties according to stringent requirements with respect to the quality of ion-exchange resins.

### GENERAL INFORMATION CONCERNING THE MANUFACTURE OF SOLID ION-EXCHANGE RESINS

The manufacture of the majority of solid ion-exchange resins includes two basic stages: 1) obtaining an insoluble polymeric matrix; 2) adding a corresponding functional group capable of ion exchange to this matrix.

The first polymerization stage is almost identical for all the types of resins and does not depend on the assignment of a resin. The basic properties of the polymer consist in hydrophobicity and its ability for swelling in a suitable organic solvent with no dissolution. On the second (“activation”) stage, a hydrophilic polymer is formed capable of swelling in water, but still being water insoluble. The nature of this stage could be varied over a wide range depending on the assignment of the resin under consideration (anion exchange or cation exchange).

About 90 % of commercial synthetic ion-exchange resins are obtained on the basis of polystyrene, *i. e.* the product of styrene polymerization. However, solid polystyrene can be dissolved in organic solvents (aromatic and chlo-

ro-substituted hydrocarbons), whereas after introduction hydrophilic groups therein it can be dissolved in water. In order to prevent the mentioned effect, styrene is introduced with a second monomer for cross-linking. Such a monomer, as a rule, is presented by divinylbenzene (DVB). The commercial DVB represents the mixture of DVB and ethylstyrene, each of those contains meta and para isomers.

For the last years, diethylbenzene obtained *via* disproportionation method is used for DVB manufacture. In this connection, the contribution of para isomers to DVB isomers has increased. So, if earlier the mass fraction of meta isomer in commercial DVB was 3.1–3.3 times higher than the mass fraction of para isomer, now the mentioned ratio amounts to (1.8–2.0 : 1.0). The rate of DVB para isomer polymerization is higher than it is for meta isomer, therefore a more rigid and irregular structure of copolymer is formed in the course of the synthesis, with great internal stress values at separate sites. This fact exerts a negative influence upon the osmotic stability level of the ionite prepared, thus the latter cannot withstand stresses those occur in changing the volume of granules, both at the stages of synthesis, and in the course of operation.

When obtaining anion-exchange resins based on styrene-DVB copolymers of various modifications (gel, macroporous, isoporous), the “activation” stage involves the two stages such as

chloromethylation and amination [1]. The first stage is determining, since the chloromethylation conversion level determines the properties of anionites, first of all their exchange capacity with a high enough osmotic stability, *i.e.* the stability with respect to the destruction under the action strong osmotic shock.

Chloromethylation consists in the direct substitution of a hydrogen atom by chloromethyl group  $\text{CH}_2\text{Cl}$  [2]. In the course of synthesizing anionites the process of chloromethylation occurs at the carbon atom of the aromatic ring composing the basic cell of styrene-DVB copolymer [3]. At the second stage consisting in the amination of chloromethylated styrene and DVB copolymer (CMC) by suitable amine, chlorine atom substitution by functional amino group occurs. When obtaining strongly basic monofunctional anionite AV-17, trimethylamine is used for amination to substitute a chlorine atom by quaternary ammonium group  $\text{N}(\text{CH}_3)_4$  [4].

#### MANUFACTURE OF STRONGLY BASIC ANIONITE AV-17

The method of chloromethylation with the use of  $\text{ZnCl}_2$  employed for manufacturing the strong-basic anionite AV-17 at the Kemerovo Azot JSC exhibits a number of disadvantages connected with a high hygroscopicity of a catalyst, one-step supplying the catalyst and chloromethylation agent to the reactor, a non-op-

TABLE 1

Chloromethylation kinetics for styrene and DVB copolymer under tested conditions

Variants	Catalysts	$\omega^*$ , %	Catalyst feeding method	
1	$\text{ZnCl}_2$	100	Copolymer + catalyst	
2	Zn-containing complex	100	From above	
3	$\text{ZnCl}_2$	50	Copolymer + catalyst	
4	Zn-containing complex	50	From above	
5	«	«	50	From below
6	«	«	25	From above
7	«	«	25	From above
8	«	«	25	From below
9	«	«	25	From below

\* Angular rotation velocity (% of the nominal rotation velocity of the stirrer in the reactor).

timum mode of reaction mass stirring, *etc.* These factors exert a negative effect on the quality of the finished product according to such parameters as mechanical strength and osmotic stability, since an intense course of the reaction under existing conditions could promote the formation of cracks on the surface of anionite granules.

The method we have suggested for obtaining anionite with the use of zinc-containing complex as a catalyst under certain conditions allows one to improve the quality of the finished product.

We have studied the influence of chloromethylation conditions (such as the reaction mass stirring intensity, the method of feeding the reactor with the catalyst and chloromethylation agent, the duration time of the process, the use of classical  $ZnCl_2$  catalyst and zinc-containing complex) upon the mechanical strength, osmotic stability and technological properties of strongly basic anionite.

As the initial raw material we used commercial standard styrene and DVB copolymer with the «linking» level amounting to 8 % (Russia) obtained on the basis of technical-grade DVB with the ratio between meta and the para isomers, equal to 2 : 1. The chloromethylating agent was presented by monochlorodimethyl ether (MCDME) released by the workshop of ion-exchange resins at the Kemerovo Azot JSC. As catalysts, we have chosen crystalline  $ZnCl_2$  and

a zinc-containing complex especially obtained at the workshop of ion-exchange resins of the Kemerovo Azot JSC.

The analysis of a styrene and DVB copolymer sample with respect to the basic quality parameters has demonstrated that the specific volume of limiting swelling in toluene amounts to  $2.7 \text{ cm}^3/\text{g}$  after 2.75 h, whereas this value for MCDME is equal to  $2.60 \text{ cm}^3/\text{g}$  after 30 min; the content of the main fraction with the size of 0.315–0.8 mm amounts up to 97 %.

Industrial trial tests were performed at the workshop of ion-exchange resins of the Kemerovo Azot JSC concerning the chloromethylation of styrene and DVB copolymer by MCDME employing the catalysts mentioned above with changing the method of loading the catalyst and chloromethylating agent, angular rotation velocity of the stirrer, duration time of the process, as well as obtaining the commercial anionite AV-17-8. In total, nine variants of the process have been realized; each of them was used for studying the kinetics of chloromethylation.

In the variants 1 and 3, we used a classical  $ZnCl_2$  catalyst and a traditional method of loading the reagents into the reactor: consecutive volume loading firstly copolymer, then the catalyst and MCDME. Other variants were carried out with the application of zinc-containing complex which was dosed into the reactor

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Chlorine content in CMC, mass %

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Chloromethylation time, h

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2	4	6	8	9	10	11	12	13	14
9.27	10.89	13.50	14.8	16.01	16.21	16.57	16.90	–	–
9.13	10.36	12.36	14.92	15.24	15.70	16.12	16.56	–	–
8.93	13.94	14.21	14.64	15.05	15.14	15.45	15.60	15.86	16.58
8.50	12.02	14.04	14.79	15.09	15.24	15.77	15.98	16.24	16.66
6.91	12.07	14.10	14.42	15.49	16.18	16.97	–	–	–
5.89	9.81	12.50	14.20	15.11	15.55	15.68	15.89	–	–
5.90	9.57	12.00	14.10	14.78	15.30	15.50	15.71	15.95	–
3.10	8.37	11.00	13.20	14.50	15.10	15.72	16.01	16.18	–
3.19	8.12	10.87	12.95	14.57	15.00	15.61	15.97	16.05	–

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TABLE 2

Quality indices for strongly basic technical grade anionite AV-17-8

Variants	Residual chlorine content, mass %	Mechanical strength according to Chatillon, g per granule	Osmotic stability level*, %
1	0.39	720	96.6
2	0.57	730	96.8
3	0.32	860	96.6
4	0.43	800	96.4
5	0.43	810	99.1
6	0.50	805	98.3
7	0.64	801	97.0
8	0.42	989	100.0
9	0.45	967	99.6

\* Percentage of whole granules after osmotic shock.

from above (variants 2, 4, 6 and 7) or from below (variants 5, 8 and 9) evenly during the first 4 h of chloromethylation. The duration of chloromethylation was varied within the range of 12–14 h; the process temperature did not exceed 55 °C.

The averaged results of the tests are presented in Table 1.

The process of CMC amination was carried out according to the operating production schedule for the manufacture of anionite AV-17-8 [5]. Quality parameters for technical grade anionite are presented in Table 2.

It can be seen that the use of  $ZnCl_2$ , of the usual reagent-loading method (variants 1 and 3) and a high rate of stirring does not result in the uniform chloromethylation of the copolymer. The process, especially during the first hours, proceeds very intensively, which exerts a negative effect on the mechanical strength and osmotic stability of the commercial anionite. The uniform batching (for the first 4 h) of the zinc-containing complex into the reactor, both from above (onto the surface of the reaction mass), and from below (into the bulk of the reaction mass) at the same rotation frequency of the stirrer promotes a “softer” course of the process. As a consequence, the mentioned mode provides an increase in the stability of the granules of finished anionite under the influence of a strong osmotic shock (variants 2 and 5). At the minimal intensity of stirring and all other factors being equal the use of the zinc-containing complex (variants 6–9) resulted in obtaining

the best results with respect to the mechanical strength and osmotic stability of the anionite.

Basing on the data obtained one could assume that a central whirlpool is formed at the maximal rotation frequency of the stirrer in the chloromethylation reactor. As a result, there is the stirring of the liquid phase only in the central part of the reactor with the rotation of the copolymer mass near the walls, i.e. there is no necessary stirring of all the reaction mass observed. As a consequence, the content of chlorine in CMC during the first hours of chloromethylation sharply grows, which exerts a negative effect on the quality parameters of commercial anionite AV-17-8 (osmotic stability and mechanical strength). The most uniform chloromethylation is achieved at the minimal rotation frequency of the stirrer and with the use of the zinc-containing complex as a catalyst.

In order to determine the influence of chloromethylation conditions upon such technological anionite parameter as the specific water consumption for washing, we have performed washing the averaged anionite samples obtained either by the classical method or with the use of the zinc-containing complex. The samples were washed by  $H^+$ -cationized water up to obtaining the specific electrical conductivity of the filtrate equal of to 1.5  $\mu S/cm$ , after regenerating them by sodium hydroxide. The results of the experiments are presented in Table 3. It can be seen that in the case of washing the samples of anionite obtained at the minimal stirring intensity with the use of the zinc-contain-

TABLE 3

Washing AV-17-8 anionite with H<sup>+</sup>-cationized water after the regeneration by sodium hydroxide with the specific consumption of 100 % NaOH equal to 120 kg/m<sup>3</sup>

Variants	Specific electrical conductivity of filtrates, μS/cm												
	Specific consumption of H <sup>+</sup> -cationized water, m <sup>3</sup> /m <sup>3</sup>												
	6	7	8	9	10	11	12	13	14	15	20	30	40
1, 3	4.2	2.6	2.5	1.9	1.9	1.7	1.6	1.6	1.3	1.4	1.4	1.4	1.4
8, 9	2.9	2.5	2.0	1.6	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.2	1.1

Note. Specific electrical conductivity of initial washing water amounted to 3.4 μS/cm.

TABLE 4

Main analytical parameters for mixed action filters (MAF) operating in parallel in the water treatment plant employing the anionite with improved kinetic properties (MAF pos. 1) and the traditional anionite AV-17-8 (MAF pos. 2)

Water before processing in MAF			MAF pos. 1			MAF pos. 2						
Content, mg/dm <sup>3</sup>			Number of filtration cycles	V, m <sup>3</sup>	Content, mg/dm <sup>3</sup>			Number of filtration cycles	V, m <sup>3</sup>	Content, mg/dm <sup>3</sup>		
SiO <sub>2</sub>	Na <sup>+</sup>	Fe <sub>total</sub>			SiO <sub>2</sub>	Na <sup>+</sup>	Fe <sub>total</sub>			SiO <sub>2</sub>	Na <sup>+</sup>	Fe <sub>total</sub>
–	n/d	–	1	11 966	0.008	–	–	1	11 013	0.005	–	–
–	n/d	0.018		16 236	–	–	–		17 794	–	–	–
0.037	n/d	–		28 720	–	–	–		30 322	0.013	–	–
0.036	0.32	–		35 600	–	–	–		37810	0.012	0.01	–
0.019	0.23	–		42 592	–	–	–		40 690	0.032	0.013	–
0.059	n/d	–		44 598	–	–	–	Regeneration				
0.042	n/d	–		55 544	–	–	–	2	2641	–	–	–
0.025	n/d	–		61 232	–	–	–		10 585	–	–	–
–	0.75	–		66 248	–	0.01	–		19 489	–	0.01	–
0.039	n/d	–		73 265	–	–	–		37 325	0.043	0.015	–
0.034	n/d	–		74 871	–	–	–	Regeneration				
0.028	0.63	–		75 802	–	–	–	3	3737	–	0.01	–
0.029	n/d	–		79 858	–	–	–		10 801	0.022	–	–
0.033	n/d	–		85 154	–	–	–		42 709	0.029	–	–
0.034	n/d	–		87 269	0.016	–	–	Regeneration				
0.023	0.3	–		88 298	0.019	0.01	–	4	17 477	–	0.01	–
0.051	n/d	–		88 903	0.038	0.01	–		27 445	–	–	–
0.03	n/d	–	Regeneration						43 623	–	–	–
0.053	n/d	–	2	26 610	0.012	–	–		53 980	0.153	0.01	–
0.038	n/d	–		29 497	0.012	–	–	Regeneration				
0.021	n/d	–		33 546	–	–	–	5	2543	–	–	–
0.058	0.37	–		42 618	–	0.0062	–		15 239	0.012	0.0056	–
4.45	n/d	–		51 642	–	–	–		27 479	0.015	–	–
0.03	n/d	–		62 962	–	–	–		29 231	0.02	–	–
0.03	n/d	–		79 000	–	–	–		38 341	n/d	–	–

Notes. 1. Normative quality indices for water before processing are they: the content of SiO<sub>2</sub> is less than 0.2 mg/dm<sup>3</sup>, the content of Na<sup>+</sup> being less than 0.5 mg/dm<sup>3</sup>, Fe<sub>total</sub> is not normalized; water after processing in MAF: the content of SiO<sub>2</sub> is less than 0.02 mg/dm<sup>3</sup>, the content of Na<sup>+</sup> is less than 0.01 mg/dm<sup>3</sup>, content of Fe<sub>total</sub> is less than 0.03 mg/dm<sup>3</sup>. 2. V is the volume water passed. 3. n/d – the substance was not determined, dash – the substance under determination is absent.

ing complex (variants 8 and 9), the specific water consumption for washing up to gaining the required value of the specific electrical conductivity of the filtrate is lower than for the samples obtained by the usual method with the application of  $ZnCl_2$ , amounting to 10 and 14  $m^3/m^3$ , respectively. Thus, the anionite obtained with the use of zinc-containing complex exhibits much better kinetic properties.

#### **APPLICATION OF ANIONITE AV-17-8 WITH IMPROVED KINETIC PROPERTIES**

A comparative analysis was performed concerning the potentialities and industrial testing of the ion-exchange resin specially released with the use of zinc-containing complex as a catalyst. For this purpose, we have replaced the classical anionite by the anionite AV-17-8 obtained with the use of zinc-containing complex at one of two mixed action filters (MAF) operating in parallel in the water treatment plant of ammonia producing workshop at the Kemerovo Azot JSC. Into MAF pos. 1 we have put the resin obtained with the use of the zinc-containing complex, into MAF pos. 2 we have loaded the ion-exchange resin obtained via the classical method with the application of  $ZnCl_2$ . The basic parameters of the water treatment plant operation have been registered (Table 4).

It is seen that the amount of water passed through the filter with anionite AV-17-8 obtained with the application of Zn-containing complex up to silicic acid breakthrough is 1.5-2 times higher than in the case of the usual resin. This fact indicates an increase in the filtration cycle with other things being equal concerning the operation of the filters.

Hence, anionite AV-17-8 obtained with the use of zinc-containing raw material exhibits improved kinetic properties, intense exchange kinetics with respect to silicic acid with requiring for a lower value of the specific alkali consumption for regeneration as well as of washing water for as compared to the usual anionite. The use of anionite AV-17-8 with improved kinetic characteristics allows one to lower the cost price of desalinated water to a considerable extent.

#### **CONCLUSION**

Basing on the results of industrial trial tests carried out with respect to the manufacture of anionite AV-17-8 with improved kinetic properties as well as with respect to its application in MAF for a water-treatment plant we have developed Engineering specifications TU 2227-062-05761637-2006 those provide the release of new anionite AV-17-8 grades for desalination installations, and for MAF [6].

According to the present engineering specifications the level of such anionite parameters as the volume percentage of working fraction (up to 0.4-1.25 mm, or 98-99 % against 93-95 % in accordance with the State Standard GOST [7]) and osmotic stability (up to 98-99 % against 85-92.5 % in accordance with the State Standard GOST) has been increased to a considerable extent; the scatter in the mass fraction of moisture has been reduced (down to 42-51 and 55-65 % for separate technology and MAF, respectively).

In order to improve the competition level of anionite AV-17-8 we have introduced into practice new quality parameters such as "the fraction of whole granules before the osmotic shock", "time of precipitation" for MAF anionite and a standard for the parameter "dynamic exchange capacity (DEC)" depending on the ionic anionite form as well as a facultative parameter "specific water consumption for washing".

The methods for testing regulated by the mentioned engineering specification are based on the techniques presented GOST 20301-74 with specifying the ionic form of anionite basing on the analysis of the Russian and foreign quality inspection methods performed by the Russian Heat Engineering Institute (RHEI) [8].

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